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Comparative study of non linear optical (NLO) properties of Glycine and L-Alanine doped Zinc tris Thiourea Sulfate single crystal

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ABSTRACT

Zinc (tris) thiourea sulfate (ZTS) is promising semi organic nonlinear material in the field of photonics and optoelectronics. In present investigation amino acid Glycine and L-Alanine were added in molar percent in under saturated ZTS solution to enhance second harmonic generation (SHG) efficiency. Effect of Glycine and L-Alanine on SHG efficiency has been studied by Kurtz and Perry powder test. Glycine and L-Alanine doped zinc (tris) thiourea sulfate single crystals were grown from aqueous solution by slow evaporation technique. The grown crystals were subjected for various characterizations. FTIR studies have been carried out to identify the functional groups present in the crystal. The effect of Glycine and L-Alanine on transmittance of grown crystals was studied by UV–visible study. The grown crystals were subjected to single crystal X-ray diffraction.

Keywords: FTIR, UV visible Study, X-ray diffraction.

INTRODUCTION

In last several years, there has been considerable interest in growth and characterization of nonlinear optical materials [1-4]. NLO material plays a major role in applications such as telecommunications, optical data storage and optical information processing [3-5]. Second order nonlinear optical materials are used in optical switching, frequency conversion and electro-optical applications especially in Electro Optical modulators [6]. In addition to large second order susceptibilities, good transmission in UV and visible region and stable physico thermal performance is needed for these applications [7]. Inorganic NLO materials have large mechanical strength, thermal stability and good transmittance, but modest optical nonlinearity due to the lack of extended π-electron dislocation [8]. Purely organic NLO material have large nonlinearity compared to inorganic material but low optical transparency, poor mechanical and thermal strength and low laser damage threshold [9]. Thus, the research is focused on semi organic NLO material crystal in order to obtain superior NLO crystal by combining the advantages of organic and inorganic materials.

Zinc (tris) Thiourea Sulfate (ZTS) is a promising semi-organic NLO material for second harmonic generation from metal complexes of thiourea. ZTS is 1.2 times more nonlinear than KDP [10-11]. ZTS possesses orthorhombic structure with space group $Pca2_1$ [12]. Most of the amino acids individually exhibit the NLO property. The tetrahedral array of four different groups about α-carbon confers optical activity on amino acid [13].

The effects of several dopants on structural and physical properties of metal complexes of thiourea and KDP have been reported [11, 14, 15]. Semi organic nonlinear optical (NLO) crystals formed by amino acids with inorganic materials possess the advantages of high optical nonlinearity of the organic amino acids.

METHODOLOGY

Synthesis

ZTS salt was synthesized by dissolving AR grade zinc sulfate and thiourea in deionized water according to following reaction,

$$ZnSO_4 .10H_2O + 3[CS (NH_2)_2] = Zn [CS (NH_2)_2]_3SO_4$$

The synthesized salt was purified by repeated re-crystallization. Saturated solution of ZTS was prepared at room temperature and 1, 2 and 3mole% of Glycine and L-Alanine was added in separate beakers. The synthesized salt was purified by repeated crystallization and tested for SHG by Kurtz and Perry powder test. We observed enhancement of SHG efficiency in ZTS when it is doped with Glycine and L-Alanine. Hence Glycine and L-Alanine doped ZTS crystal were grown by low temperature solution growth method.

RESULTS AND DISCUSSION

1 SHG Measurement

The study of NLO conversion efficiency of grown crystal has been carried out in accordance with the classical powder method developed by Kurtz and Perry [16]. It is an important and popular tool to evaluate the conversion efficiency of NLO materials. A Q-switched Nd: YAG laser beam of wavelength 1064 nm, with an input power of 4.5 mJ, and a pulse width of 8 ns with a repetition rate of 10 Hz were used. The crystals of pure ZTS and 1, 2 and 3mole% Glycine and L-Alanine doped ZTS was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to laser radiations. The output from the sample was monochromated to collect the intensity of 532nm component, and to eliminate the fundamental wavelength. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube. The generation of second harmonic was confirmed by the emission of green light. A sample of ZTS was used as a reference material for the present measurement. The SHG conversion efficiency of Glycine and L-Alanine doped ZTS were found to be enhanced than that of pure ZTS. The optical signal generated from sample is converted into electrical signal and was measured on oscilloscope. The measured output for pure ZTS is 35 mV. The measured output 1, 2, 3mole% Glycine doped ZTS were **145mV**, 85mV and 93mV respectively for and 1, 2, 3mole% L-Alanine doped ZTS were **61mV**, 55mV and 57mV respectively. This indicates that SHG conversion efficiency of Glycine and L-Alanine doped ZTS is greater than pure ZTS.

2 X-ray Diffraction Analysis

Single crystal X-ray diffraction analysis of grown crystal was carried by Brukers axs (Kappa Apex) diffractometer to determine lattice cell parameter. The collected data of lattice cell parameters for Glycine doped ZTS are a = 11.168 Å, b = 7.798 Å, c = 15.516 Å and cell volume = 1351.3 Å^3 and α = β = γ = 90°.

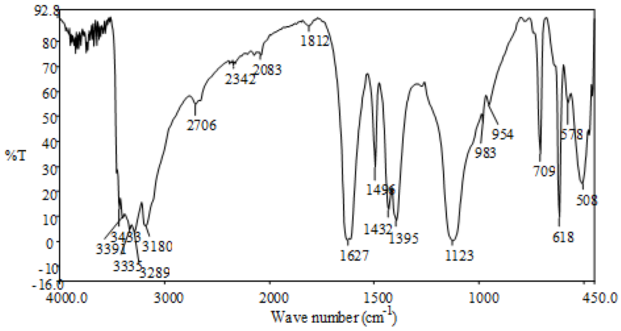

Fig.1. FT-IR spectra for pure ZTS

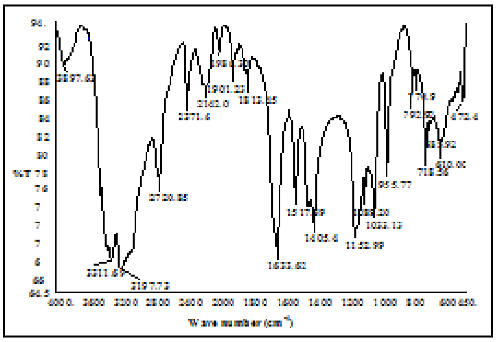

Fig. 2. FT-IR spectra for 1mole% Glycine doped ZTS

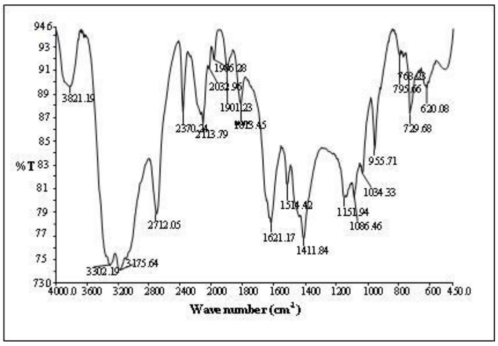

Fig.3. FT-IR spectra for 1mole% L-Alanine doped ZTS

Table 1: Comparison of IR bands of 1mole% Glycine doped ZTS with thiourea and ZTS.

Thiourea	ZTS	1mole%Glycine doped ZTS	Assignment
411	--	--	δs(N-C-N)
469	508	472	δs(C-S-N)
740	709	718	vs(C=S)
1089	1123	1089	vs(C-N)
1417	1432	1405	vas(C=S)
--	1496	1517	v(N-C-N)
1627	1627	1633	δ(NH_2)
3167	3180	3197	vs(NH_2)
3280	3289	--	vs(NH_2)
--	--	3311	vas(NH_2)
3376	3391	--	vas(NH_2)

δ – bending, v – stretching, s – symmetric, as – asymmetric.

Table 2: Comparison of IR bands of 1mole% L-Alanine doped ZTS with thiourea and ZTS.

Thiourea	ZTS	1mole%L-Ala. doped ZTS	Assignment
740	709	729	vs(C=S)
1089	1123	1086	vs(C-N)
1417	1395	1411	vas(C=S)
--	1432	--	vas(C=S)
--	1496	1514	v(N-C-N)
1627	1627	1621	δ(NH_2)
3167	3180	3175	vs(NH_2)
3280	3289	--	vs(NH_2)
3376	--	3302	vas(NH_2)
--	3391	--	vas(NH_2)

δ – bending, v – stretching, s – symmetric, as – asymmetric.

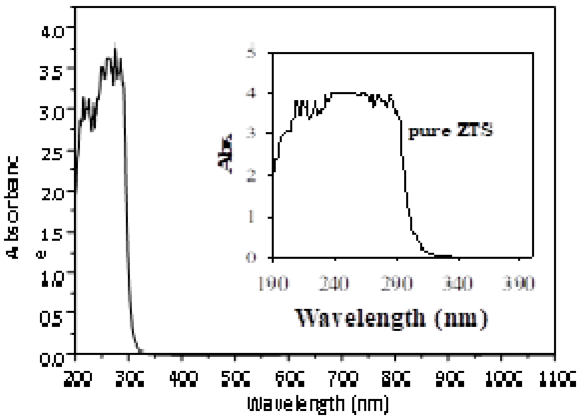

Fig. 4.

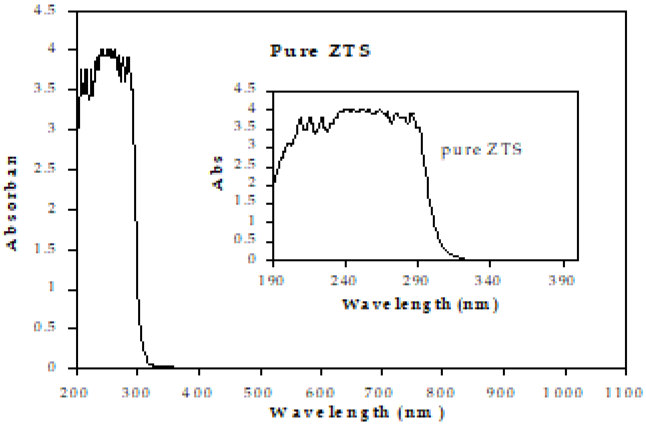

Fig. 5

Fig. 4. UV-visible absorption spectra of 1mol%Glycine doped ZTS

Fig. 5. UV-visible absorption spectra for 1mole% L-Alanine doped ZTS

The observed unit cell parameters for L-Alanine doped ZTS are a =11.159 Å, b =7.792 Å, c = 15.527 Å, cell volume = 1350.2 Å^3 and α = β = γ = 90˚. Both crystals belong to orthorhombic system with space group $Pca2_1$. From single crystal X-ray analysis it is confirmed that dopant does not changes the basic structure of crystals [15, 17]. There is slight increase in unit cell volume. This increase in volume may be due to the change in pH of the solution due to addition of amino acid [17].

4 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR analysis was carried out by Perkin Elmer Spectrum FTIR spectrometer by KBr pallet technique in the range 450-4000cm^{-1}. The FT-IR spectra of pure ZTS and 1mole% Glycine and L-Alanine doped ZTS is shown in Fig. 1 Fig. 2 and Fig. 3 respectively. In ZTS complex, there are two possibilities by which the coordination with metal can occur.

It may be either through nitrogen or through sulfur. From spectra, the N-H absorption bands in the high frequency region in thiourea were not shifted to lower frequencies on formation of metal thiourea complex, thus coordination of thiourea occurs through sulfur in ZTS [11, 12]. The comparison shows slight shift in characteristic vibrational frequencies of 1mole% Glycine and L-Alanine doped ZTS with respect to pure ZTS [17]. This confirms the addition of Glycine and L-Alanine in grown crystal.

5. UV-Visible Spectral Study

The UV-visible studies of grown crystal was carried out by Shimadzu UV 1600 UV-vis. spectrometer in a range 200 nm to 1100 nm. The absorption spectra of 1mole% Glycine and L-Alanine doped ZTS is shown in Fig. 4 and Fig. 5 respectively. The window shown in Fig shows UV spectra of pure ZTS for comparison. The absorption spectra reveal that the crystal has lower cutoff wavelength at around 290 nm. The absorption near UV region is associated with electron transition within thiourea units of ZTS. Doping of both 1mole% Glycine and L-Alanine in ZTS does not destroy the transparency of the crystal. From spectra it has also been observed that the lower cutoff wavelength is almost the same for Glycine and L-Alanine added ZTS and pure ZTS crystals [18]. The wide range of transparency in UV, visible and IR region enables good transmission of the second harmonic frequencies of Nd: YAG laser. This is an added advantage in the field of optoelectronic applications.

CONCLUSION

The 1mole% Glycine and L- Alanine doped ZTS crystal has been grown from aqueous solution by low temperature solution growth, slow evaporation technique. The Kurtz and Perry powder SHG test shows that the SHG efficiency of 1mole% Glycine doped ZTS is 4.14 times more than pure ZTS. 1mole% L-Alanine doped ZTS has SHG efficiency 1.74 times that of pure ZTS. Thus the enhancement in SHG is more for 1mole

% Glycine doped ZTS than 1mole%L-Alanine doped ZTS. Following the FTIR data one can see that the intrinsic defects in studied crystal. These defects play substantial in observed second order susceptibility and it may be main strategy to improve their nonlinear optical properties [19]. The FT-IR spectrum confirms the presence of all the functional group and presence of Glycine in the grown crystal. The powder and single crystal X-ray analysis confirms the ortho-rhombic structure of the grown crystal. UV-visible study reveals the Glycine and L-Alanine doped ZTS crystals has lower cutoff wavelength at around 290 nm. The enhancement in SHG efficiency of Glycine and L-Alanine doped ZTS is due to the optically active amino group which may get added in the structure and increases its non-Centro symmetry and hence increasing its SHG efficiency. Thus, the grown crystal is a potential candidate for optoelectronic and laser applications.

Conflicts of interest: The authors stated that no conflicts of interest.

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